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New approaches for the reactive dyeing of the retanned carbohydrate crust leather

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Abstract

A number of reactive dyestuffs of three different categories, i.e., monochlorotriazine, dichlorotriazine and vinyl sulfone have been examined with some carbohydrates, i.e., glucose, galactose and fructose in the crust leather dyeing to determine the correlation between the reactive groups of the different dyestuffs and retanned leather. These carbohydrates were used as retanning agents to develop the dye–leather affinity. There are indications that some correlation could exist and for the dyestuffs examined, pH plays an important role to give a reasonable measure for the dye–leather affinity and the behaviour of the dyestuff. The effect of carbohydrates on the mechanical properties, thermal stability and the main amino acids' content of the crust leather were investigated. The average affinity numbers of the used dyestuffs were also evaluated.

Keywords: Carbohydrates; Crust leather; Maillard reaction; Reactive dye

1. Introduction

Leather, a high value commodity in international commerce, is very often dyed with a mixture of dyes. It differs from other natural and synthetic fibres because of its three-dimensional structure. Earlier workers studied the interaction of reactive dyes with collagen and other related proteins and indicated that covalent bonds are formed between the terminal amino groups of amino acid residues, ε-amino groups of lysine, hydroxylysine, arginine or hydroxyproline of collagen and dye molecules [1,2]. A variety of chemical and physical treatments are used to convert collagen into leather by modification of its chemical characteristics and amphoteric nature. The exact mechanism may involve the interaction of the dye molecules with the reactive functional groups of collagen or a collagen–tanning complex or both. Dye uptake by leather may be attributed to specific forces of attraction, e.g., covalent, hydrogen and ionic bonding or non-specific forces such as van der waals forces [3]. Glucose and galactose are aldehydic sugars with six carbon atoms, i.e., are aldo-hexoses, while fructose is a ketonic hexose or keto-hexose. The simple sugars are characterized by the presence of carbonyl groups (either aldehydic or ketonic) and by alcoholic hydroxyl groups [4,5]. Maillard reactions occurring between L-lysine and monosaccharides were detected by L.C. Maillard in 1912 and Kurosaki et al. [6]. Chemical modification of wool, enabling enhanced dye pick-up under relatively mild process conditions, has been studied for decades. The desired improved dyeability of wool has been achieved initially via interaction with glucose derivative of crown ether. The incorporation of carbohydrates to loosen the fibre structure and build in special functional groups in order to economise on dye consumption at lower temperature was achieved [7–9]. The affinity of dye to leather depends mutually on the structure and state of both the dye and leather, for the leather, it depends on the type of tannage, the presence of chemical active substances in the float, the surface active agents on the fibre surface and the chemical modification types, while for the dye, it depends on the chemical structure

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of the dyestuffs and their sensitivity to any of the dyeing conditions [10]. The effect of the reactive dye concentrations on the colour strength of cationised leather prints investigated that low dye concentration was recommended in comparison with the untreated ones [11]. The application of dyes as tanning agents is not confined to a single dye type; it depends only on the availability of reaction sites. The class of tanning reagents starts with aldehyde derivatives of carbohydrates which were obtained by the oxidation of some carbohydrates with periodic acid. Komanovsky has effectively generalized these reactions in his studies of the reactions within collagen at low moisture content and the basis of the formation of permanent bonds depends on the Maillard reaction [12,13]. Unlike textile, leather is not a flat material of uniform thickness, but a three-dimensional substrate into which dyes can penetrate to a varying extent. Consequently, it is possible to obtain widely different surface dyeings with the same dye combination on different leathers; also, leather is a substrate with two surfaces of different affinities and accessibilities for dyes. The selection of dyes for leather dyeing depends on the nature of the tannage and the demands on dyeing, i.e., whether a surface dyeing is required (as in the case of shoe upper leather) or whether the dyes are to penetrate to a certain extent or through the entire cross-section [14] (as in clothing leather, furniture upholstery leather and glazed kid). Using of 5% retanning agents, such as synthetic polymers and vegetable tanning leads to decrease in the dye exhaustion [15]. The relationship between the type of retanning and dye affinity to leather is very important and the colouration of leather is not only dependent on the affinity of the dyestuff for leather but also on the affinity of the leather for dyestuffs [16].

2. Experimental

2.1. Materials

- Neutralized cattle crust leather (chrome tanned) was supplied from the local tannery at Cairo, Egypt.
- D(+) Glucose, D(+) galactose and D(−) fructose (99%), were supplied from BDF chemicals.
- Potassium iodate (99%), which acts as oxidizing agent, was supplied from Fluka.
- The commercial reactive dyestuffs with different chemical structures, were selected from three different reactive categories:

(I) Vinyl sulfone
  (A) Remazol Black B
  (B) Remazol Brilliant Blue R
  (C) Remazol Golden Yellow RNL
(II) Monochlorotriazine
  (D) Cibacron Yellow P6GS
  (E) Cibacron Red MX
  (F) Cibacron Marine
(III) Dichlorotriazine reactive
  (G) Procion Red MX5B
  (H) Procion Yellow MX8G
  (I) Procion Blue MX

2.2. Methods

2.2.1. Modified Maillard reaction for the retanning of crust leather [17]

Crust leather samples, *X* (indicates weight of sample) g, were treated in the aqueous solution of 10 g/l glucose at a liquor ratio 20:1. Potassium iodate in molar ratio 2:1 was then added for 40 min at 40 °C. Other leather samples were treated with galactose and fructose under similar condition. Blank treatment baths were also used as control.

2.2.2. Reactive dyeing

Treated/untreated crust leather samples, *X* (indicates weight of sample) g, were dyed with 1% dye, in a liquor ratio 1:8 at 45 °C for different time intervals (10, 20, 30 and 40) min at pH 8. Other samples were dyed in the remaining dyeing baths after the pH was changed to 5.

2.2.3. Testing and measurements

i. The colour strength (*K*/*S*) of the untreated and treated dyed samples was measured using Ultra Scan XE apparatus [18,19].
ii. Colour fastness to the artificial light was tested according to DIN [20].
iii. Scanning electron micrographs of both surface and cross-section of the untreated and treated samples were recorded using Jeol JXA-840A scanning electron microscope.
iv. FT-IR spectra of the untreated and treated crust leather powder samples were recorded using Perkin Elmer spectroscopy.
v. The effect of the carbohydrate reaction on the main amino acid constituents of the treated crust leather in comparison with the untreated sample was determined using Eppendorf − LC3000 amino acid analyzer.
vi. According to Haroun et al. [21,10], the degree of the dye penetration was calculated using light microscope.

2.2.4. Determination of the affinity number [22,23]

Treated/untreated crust leather samples, *X* (indicates weight of sample) g, were dyed with 1%, 3%, 5%, 7% and 9% Remazol Black B and Remazol Brilliant Blue R, in a liquor ratio 1:8 at 45 °C using different time intervals (10, 20, 30 and 40) min. A first series of tests is carried out at pH 8, followed by the second series in the remaining dye bath at pH 5. The affinity number was calculated using Eq. (1).

$$\text{Affinity number (AN)} = \frac{(\%E)_{\text{pH 8}} + (\%E)_{\text{pH 5}}}{2} \quad (1)$$

$$\%E\ \text{(dye uptake)} = \frac{(\text{Ab})_{\text{a}} - (\text{Ab})_{\text{b}}}{(\text{Ab})_{\text{b}}} \times 100$$

Where, $(\%E)_{\text{pH 8}}$ is the dye bath exhaustion percentage at pH 8, $(\%E)_{\text{pH 5}}$ is the remaining dye bath exhaustion

percentage at pH 5, $(Ab)_a$ is the absorbance of the dye solution after certain dyeing time, and $(Ab)_b$ is the absorbance of the dye solution before the dyeing process.

2.2.5. Determination of the dye chemical potential [24]

In case of the two vinyl sulfone reactive dyes, i.e., Remazol Black B and Remazol Brilliant Blue R, *X* (indicates weight of sample) g of crust leather was added to 15 ml distilled water and 25 ml dye solution (1%) in dialysis tube placed in constant temperature water bath (28 °C), gently rocked and allowed to attain equilibrium over 4–7 days. The dye–leather energy was calculated from the concentration of the used dye in the substrate and in the solution at the equilibrium condition from Eq. (2).

$$-\Delta\mu^{o} = RT \ln\frac{[D]_f}{[D]_s}\ \mathrm{kJ\,mol^{-1}} \quad (2)$$

Where, $-\Delta\mu^{o}$is the differences in the chemical potential of the dye in the solution to fibre (crust leather) at equilibrium condition, R is the gas constant (0.0821 atm. $grd^{-1}\,mol^{-1}$), *T* is the absolute temperature ($t\,^{\circ}C + 273$), $[D]_f$ is the dye concentration in the fibre (crust leather), and $[D]_s$ is the dye concentration in the dyeing bath solution.

3. Results and discussion

Fig. 1 shows FT-IR spectra of the hide powder and glucose retanned hide powder. The spectra illustrated that the significant differences between the two spectra could be detected. The vibration band at 999 cm^{-1} corresponds to the glucose molecule and the band at 1250 cm^{-1} corresponds to N–C bond in the condensation reaction between the amino groups of the collagen and the aldehyde groups of the glucose.

Fig. 2 shows SEM micrographs of the grain surface and cross-section of the carbohydrate retanned crust leather in comparison with the untreated one. The grain surface of the retanned crust leather with glucose was more full and the pores were closed relative to the other treatment (fructose) and the untreated samples. While, in case of fructose treatment, the grain surface was more soft and well coated. On the other side, the fibre bundles of the retanned crust leather with carbohydrate were splitting up more and swelling in comparison with the untreated sample.

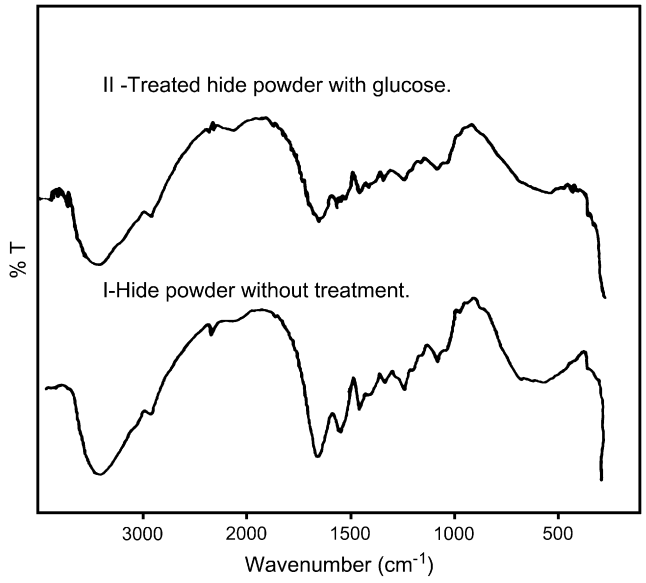


Fig. 1. FT-IR spectra of the untreated and treated hide powders with glucose.

Fig. 3 shows the effect of glucose, galactose and fructose treatment on the thermal stability of the crust leather. The data illustrated that use of different types of carbohydrate have the same influence on the shrinkage temperature of the retanned crust leather in comparison with the untreated sample; in other words, the thermal stability of the retanned crust leather with glucose, galactose and fructose was improved, this may be due to the same condensation reaction taking place between these carbohydrates and the amino groups of the collagen.

Fig. 4 shows the influence of glucose treatment on the major amino acids' content of the crust leather. The data illustrated that the assumed condensation reaction between the amino group of the amino acids and the aldehyde group of the glucose caused a marked drop in amino acids' content which means that the proline, glycine and alanine content decreased by 33.6%, 78.2% and 22.9%, respectively, while the arginine content slightly altered. The Maillard reaction with glycine was more definite than that with arginine, alanine and proline, respectively, this may be because of the reason that chrome tanning of collagen (matrix of leather) was done at proline with high possibility than that at glycine; in other words, the Maillard reaction takes place more easily at glycine. This is a useful indication of the location of the Maillard reaction within the structure of leather, as shown in Scheme 1.

Table 1 shows the effect of glucose on the mechanical properties of the dyed crust leather with the three different reactive dye categories. The data illustrated that simultaneously occurring changes in the selected characteristics of the dyed crust leather (tensile strength and elongation at break) was caused by pretreatment with glucose. Generally, both tensile strength and elongation at break of glucose retanned and dyed crust leather were improved relative to the untreated samples. This was expected, from the fact that Maillard reaction provides high fullness and compact collagen fibres.

Fig. 5 shows the effect of the carbohydrates on the dye penetration through dyeing of the crust leather with 1% of the three reactive categories. The curves illustrated that the treatments increase the fibre diameter which led to raise in the rates of dye penetration and diffusion. Consequently, the time needed to achieve good quality dyeings could be reduced. The modified Maillard reaction allowed the carbohydrate molecules to build up between peptide chains, causing an increase in swelling and hence penetration of dye into the crust leather. The accessibility and number of sites for reactive dyes were thus increased. New primary alcoholic hydroxyl groups were introduced into crust leather, as shown in Scheme 2. The reactive dyes of the three categories (monochlorotriazine, dichlorotriazine and vinyl sulfone) were used to test this hypothesis.

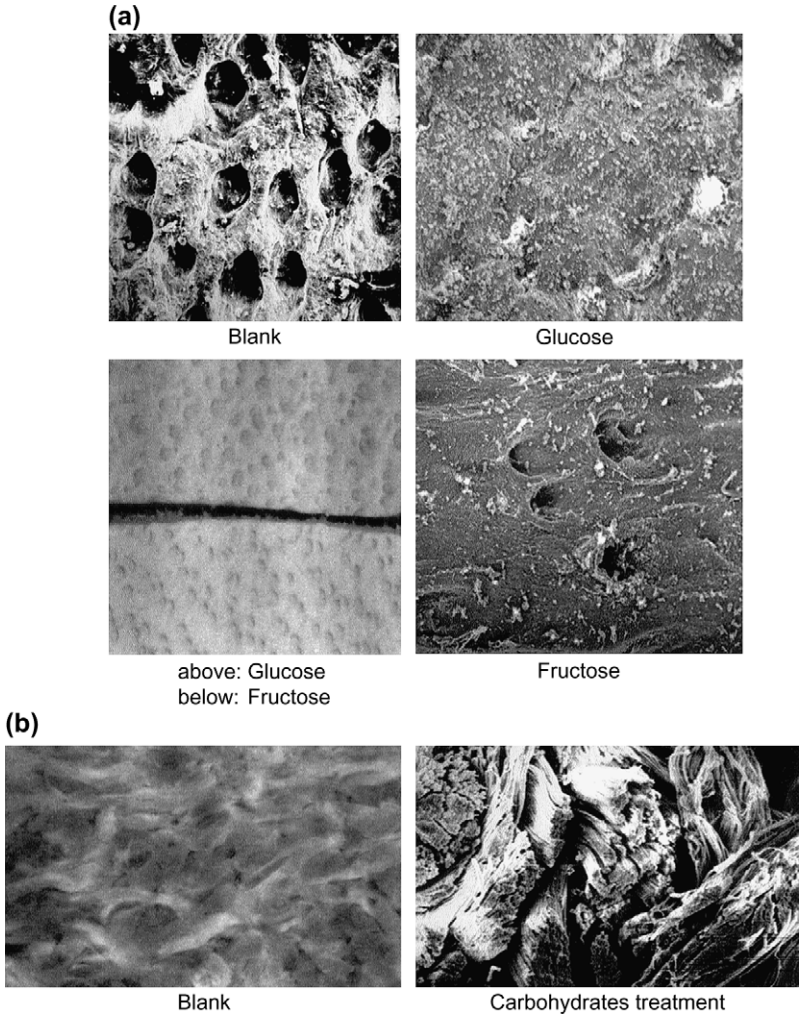


Fig. 2. SEM micrographs (200×) of the untreated and treated crust leathers: (a) grain surface and (b) cross-section.

Figs. 6 and 7 show the effect of carbohydrates on the colour strength and dye exhaustion percentage of the dyed crust leather with the three reactive categories, respectively. The curves illustrated that both colour strength and dye exhaustion were increased in comparison with the untreated samples, this may be due to the fact that the accessibility and number of sites for reactive dyes were increased. This effect leads to an increase also in dye fixation. Chrome tannage, introduces additional cationic charges. In chrome tanning, collagen develops a high affinity for all anionic dyes whose isoelectric point (IEP) is just below 7. When leather is immersed in the dye bath, dyeing takes place in three stages: (1) transfer of dye from the solution to the surface of the substrate, (2) adsorption of dyestuff at the leather surface and (3) diffusion of dye from the leather surface to its interior. In general,

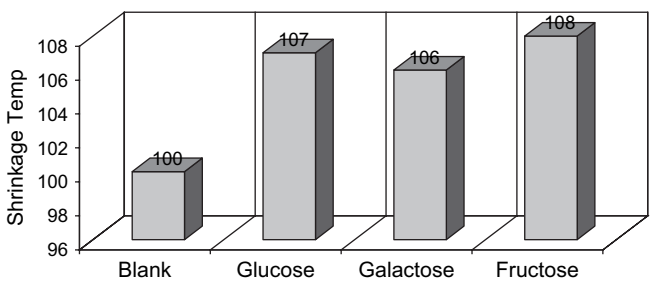


Fig. 3. Effect of some carbohydrates on the thermal stability of the crust leather.

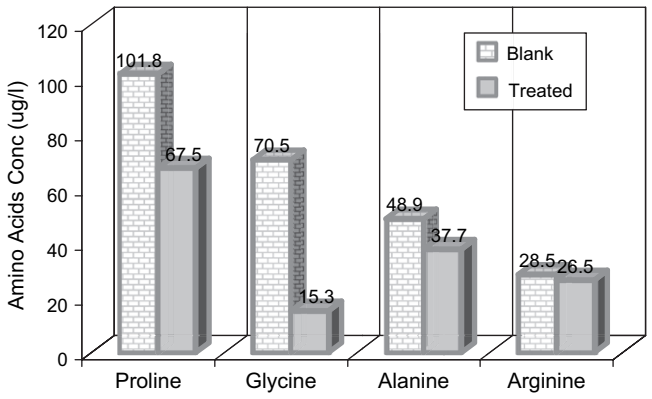
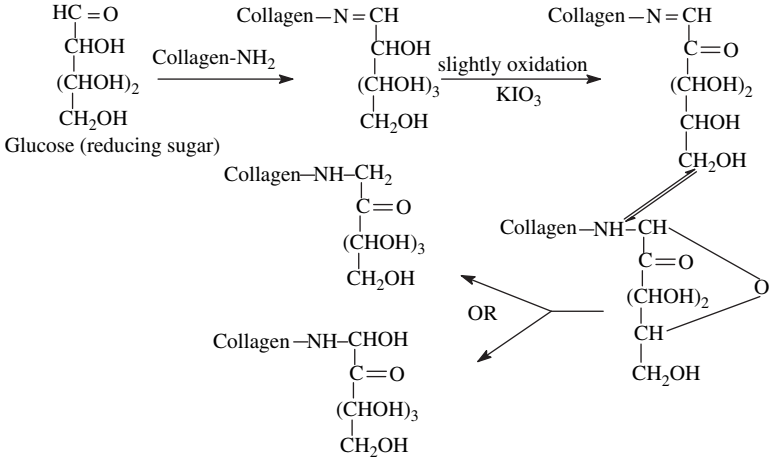


Fig. 4. Effect of glucose on the major amino acids' content in the crust leather.



Scheme 1. The expected Maillard reaction mechanism of the crust leather.

dyeing consists of partition of the dye between leather and dye bath, and so, for economical dyeing there must be good exhaustion of the dye bath.

Table 2 shows the effect of carbohydrates on the light fading of the dyed crust leather with the three reactive categories. The data illustrated that the light fastness of carbohydrate retanned and dyed crust leather was improved in comparison with the untreated samples. This may be due to the well-distributed carbohydrate molecules on the retanned crust leather surface which prevent the aggregation of the dye molecules. This means that the decrease in light fading was accompanied by an improvement in the light fastness.

3.1. Reactive dye–leather affinity

In general, dyeing may be considered from two aspects; the kinetic aspect which is concerned with the rate of adsorption of dyes and the thermodynamic aspect which examines the distribution of dye between leather and dye bath when equilibrium has been established. However, leather dyeing is not simply like collagen dyeing, it involves dyeing tanned collagen and the nature of tanning and retanning greatly influences the dye–fibre interactions, and so, the affinity of leather is the result of the affinity of collagen and of all chemical operations which are being applied to bring hide or skin to the required state of the finished product. This varies within large limits and these limits are given by specifications for the end product. Reactive dye–leather affinity may be defined as the difference in the chemical potential of the dye in the specified standard state in the solution to fibre. Quantitative studies of dyeing equilibrium are useful for investigating the nature of absorption process through the determination of dye–leather affinity which was calculated from Eq. (2). The results are given in Fig. 8. In case of Remazol Black B, the affinity was increased till 2.0–3.0 mg/l dye concentration, while in case of Remazol Brilliant Blue, the affinity was increased till 5.5–7.0 mg/l dye concentration. This may be due to the difference in the physical behaviour of the two dyes, like, the steric hindrance and the rate of dye molecules' aggregation. It can be concluded that reactive dyeing of the chemically modified crust leather with two different vinyl sulfone reactive

Table 1
Effect of glucose on the mechanical properties of the dyed crust leather

Dye types	Modification	Mechanical properties	
		Tensile strength (kg/cm^2)	Elongation at break (%)
Remazol Black B	Blank	124	54
	Treated	225	57
Cibacron Marine	Blank	153	80
	Treated	183	100
Procion Red MX5B	Blank	139	61
	Treated	189	75

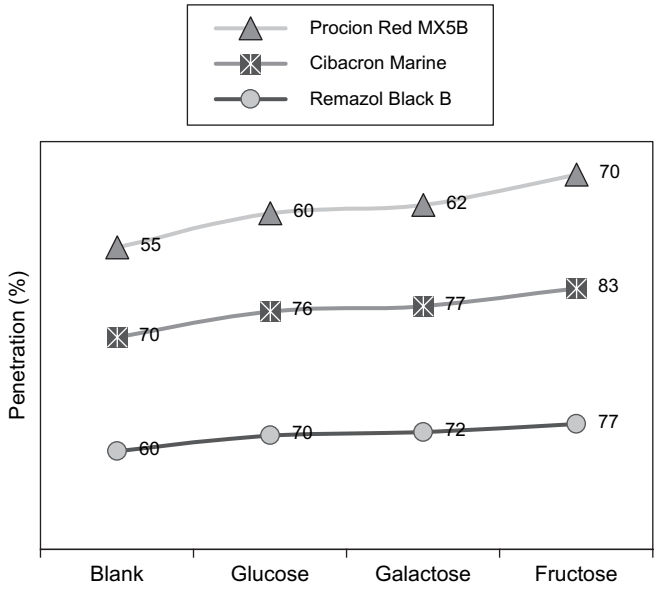
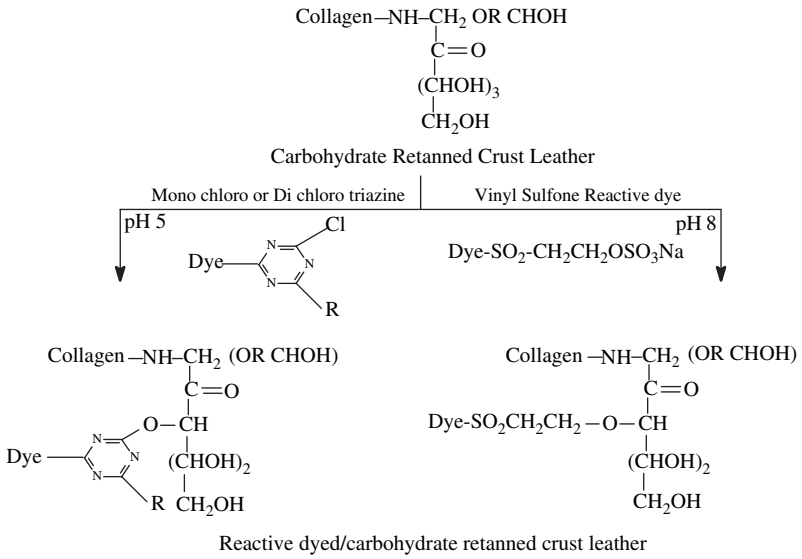


Fig. 5. Effect of carbohydrates on the dye penetration through dyeing of the crust leather with the three reactive categories.



Scheme 2. The proposed reactive dyeing of the carbohydrate retanned crust leather.

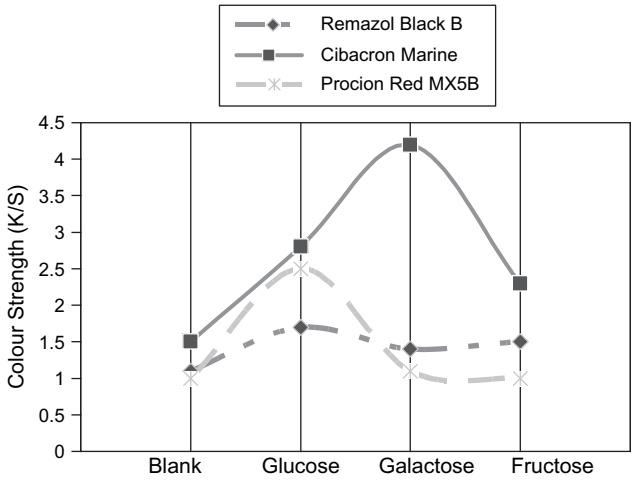


Fig. 6. Effect of carbohydrates on the colour strength of the dyed crust leather with the three reactive categories.

Table 2
Effect of carbohydrates on light fading of the dyed crust leather with the three reactive categories

Dye types	Modification type			
	Blank	Glucose	Galactose	Fructose
Remazol Black B	3	4	4	4
Cibacron Marine	3	3–4	3–4	3–4
Procion Red MX5B	2	2–3	2–3	2–3

dyes distinguished the difference in the dye–leather affinity, in spite of the same dyeing condition and the reactive group.

Figs. 9 and 10 show the effect of time on the reactive dye–carbohydrate retanned crust leather affinity. The curves illustrated that the dye affinity was increased with prolonged time through all the used reactive categories. However, the average affinity number of the three reactive dye categories was increased in the order:

Vinylsulfone > monochlorotriazine > dichlorotriazine.

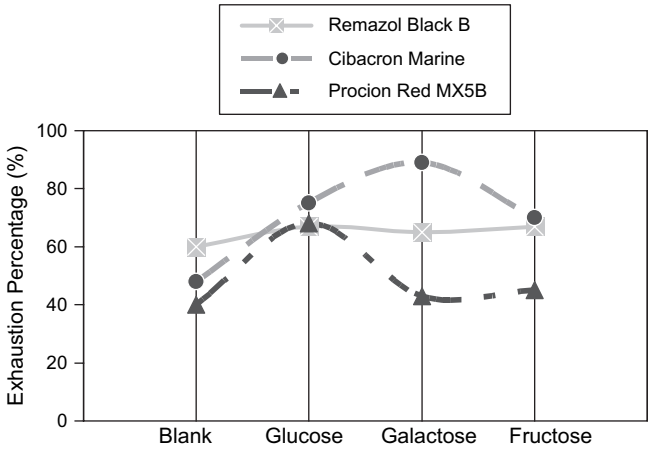


Fig. 7. Effect of carbohydrates on the dye exhaustion percentage of the dyed crust leather with the three reactive categories.

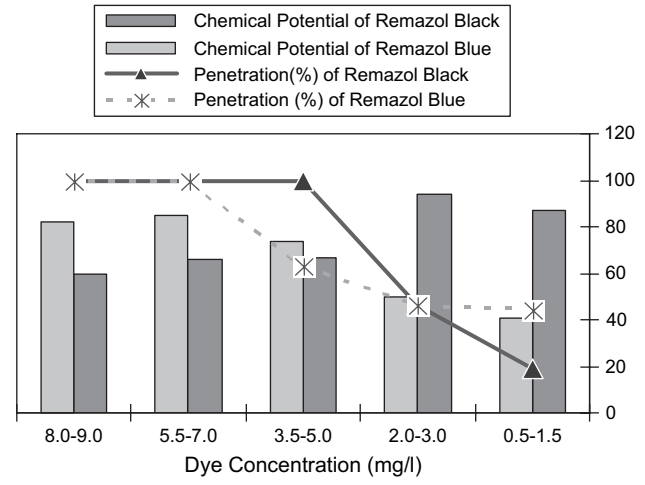


Fig. 8. Effect of dye concentration on the retanned crust leather.

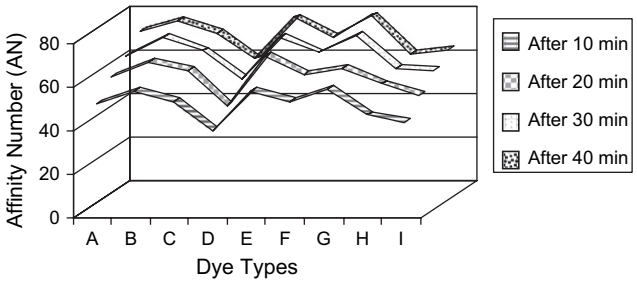


Fig. 9. Effect of time on the dye–carbohydrate retanned crust leather affinity. A: Remazol Black B; B: Remazol Brilliant Blue R; C: Remazol Golden Yellow RNL; D: Cibacron Yellow P6GS; E: Cibacron Red MX; F: Cibacron Marine; G: Procion Red MX5B; H: Procion Yellow MX8G; I: Procion Blue MX.

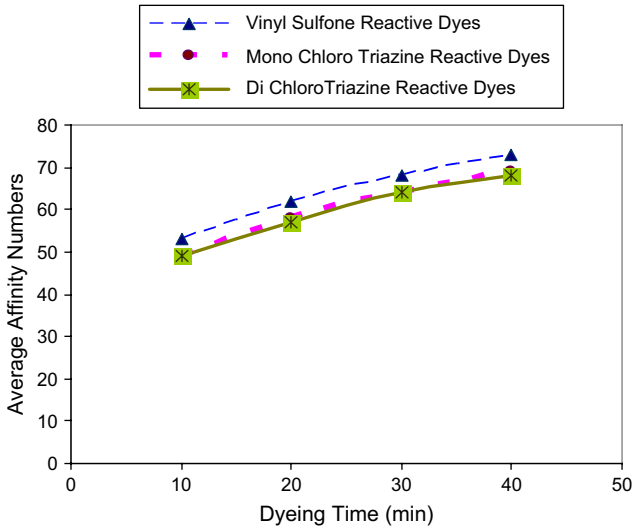


Fig. 10. Effect of time on the average affinity of the three reactive categories.

4. Conclusions

Studies on the reactive dyeing of chemically modified collagen, i.e., carbohydrate retanned crust leather, confirm the interactions between the carbohydrate and the reactive dye molecules in addition to the reaction between collagen and dyestuff. They also provide indirect evidence for the involvement of certain functional groups during the uptake of dyes. There is no single satisfactory method; a whole range of tests is needed to characterize the reactive dyestuffs. One distinguishes between those which provide a precise information of the chemical characteristics of the reactive dyestuff from those giving access to its physico-chemical behaviour towards the leather. The application of the modified Maillard reaction has succeeded in achieving considerable increase in reactive dye uptake. Carbohydrate retanning caused slight fibre swelling without deterioration of physico-mechanical properties of crust leather and also offered practical and economic benefits in leather dyeing.

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